

## Carbon Black-Polymer Interaction: A Measure of Reinforcement\*

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### Synopsis

The interaction of carbon blacks with high polymers during the mixing process was studied by using fillers having a wide range of surface characteristics. Glass beads, Graphon, high-structure blacks, and heat-treated blacks were mixed with elastomers in the Brabender Plasticorder. With the use as a rubber matrix of a high polymer that did not materially change during the mixing process in molecular weight or viscosity, excellent correlation was found between final torque required for mixing and black structure and between peak torque and bound rubber. Increasing interaction was shown to lead to increased mixing torque, increased Mooney viscosity, increased modulus, and higher state of cure, as measured by swelling. If the high polymer matrix breaks down during the mixing process these influences of interaction are mostly obscured by diminishing molecular weight.

### INTRODUCTION

The reinforcement of rubber by carbon black is a well-recognized but little-understood phenomenon of present-day rubber technology, especially when the term "reinforcement" is used to mean increased resistance to tension strains or abrasive stresses. That it is important is attested to by the parallel growth of the carbon black industry and synthetic rubber usage in the past twenty years. During this period many new types of carbon black have been developed, chiefly with the aim of increasing the reinforcement potential of the black. Research to measure and explain this reinforcement potential has been intense and includes extensive work on the chemical and physical properties of the black, such as surface group and ultimate analysis,<sup>1-5</sup> "structure" or chain formation as evidenced in electron microscopic examination,<sup>2,3</sup> and by oil absorption or compressibility; and adsorptive properties such as moisture adsorption,<sup>7</sup> as well as measurement of interaction with polymer, (carbon gel, or bound rubber).<sup>8-10</sup> Examination of vulcanizates has also been used, the well-known Mullins effect<sup>11</sup> and dispersion<sup>12</sup> being two of the many approaches. Briefly it can be stated that the factors influencing reinforcement (i.e., increases in

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tensile strength, tear resistance, abrasion resistance, and modulus far beyond the values expected on the basis of the Einstein-Guth and Gold theory) are the following: (1) the extent of the interface between polymer and solid filler, which can be expressed in square meters per gram of filler or rather per cubic centimeter of compound; (2) the nature of this surface, in other words, its specific activity evident in the adsorption properties and chemical reactivity; (3) the shape of the filler particles, or the filler "structure"; (4) the porosity of the filler particles, a minor factor in most cases.

As far as surface area is concerned, a certain minimum is necessary before any practical reinforcement may be expected. This minimum is of the order of 10–20 m<sup>2</sup>/cm.<sup>3</sup> of compound.

The specific surface activity and the structure effect of blacks usually vary simultaneously and are difficult to separate. A method of separating these two is to heat the black to a temperature in excess of 1600°C. It has been shown<sup>2,14</sup> that at this temperature the reinforcing properties of a black are changed drastically and that this change is completed when heating is carried out at higher temperature.

This is illustrated in Table I for two ISAF blacks of different structure which have been heated to 3000°C. for 1 hr. This treatment removes all surface groups and graphitizes the carbon surface to a considerable extent so that it loses most of its strongly adsorptive capacity but leaves the shape factor of the particles practically unchanged.

TABLE I  
Effect of Graphitization of Black on Properties in SBR-1500

	High structure ISAF		ISAF	
	Original	Graphitized	Original	Graphitized
Surface area (N <sub>2</sub> ), m. <sup>2</sup> /g.	116	86	108	88
Oil absorption, cc./g.	1.72	1.78	1.33	1.54
H <sub>2</sub> O adsorption, (55% R.H., %)	2.4	0	1.85	0
Bound SBR, %	34.4	5.6	30.6	5.8
Extrusion shrinkage, %	30	37.5	39.6	43.5
Mooney viscosity (212°F.)	83	87	73	76
Scorch (275°F.), min.	10.5	17	18	20
Dispersion, %	99	99	99	98.2
Tensile strength, psi	3800	3400	4000	3300
300% Modulus, psi	2100	510	1500	420
Abrasion loss, cc./10 <sup>6</sup> rev.	62	181	67	142
Elongation, %	450	730	630	750
Hardness, shore AZ	73	68	68	65
Hysteresis	0.204	0.297	0.238	0.315

The data show that the graphitization has not greatly reduced the surface area nor has it reduced at all the structure as indicated by the oil absorption which measures the void volume. Actually there is a small increase in the oil absorption values. However, the vulcanizate properties in SBR-1500, using a normal tread formulation, have undergone tremendous reductions.

Not only has the tensile strength been reduced by some 10–15%, but modulus and abrasion resistance have been reduced by a factor of 3 or 4.

This dramatic change which is coupled with some minor trends of longer scorch time and higher hysteresis must be due to the loss in adsorptive properties of the black. This effect is shown by the decrease in water adsorption at 55% R.H.; changing from 2% moisture adsorption in the original blacks to zero after graphitization. More important for its significance in rubber, the percentage of bound rubber drops from approximately 20% to very low values after graphitization.

Therefore, it seems clear that the reinforcing properties reflected in modulus and abrasion resistance are determined primarily by the adsorptive activity of the black surface and not so much by the structure, indicated by oil absorption (void volume). In other words, a high-structure black does not give high modulus in a rubber vulcanizate because the structure is high but because the specific surface activity is high which usually goes together with high structure.

It is for this reason that the present study was made using bound rubber and the related shearing force necessary to mix the rubber-black compound as a measure for the surface activity.

The Guth-Gold<sup>13</sup> relationship predicts the increase in viscosity when a filler spherical in shape is wetted and dispersed in a vehicle at various volume fractions. Variation from the relationship leading to higher-than-normal viscosity may be attributed to either interaction of filler with vehicle or nonspherical filler particles, or both. It is known that reinforcing carbon blacks depart markedly from a spherical configuration.<sup>2,6</sup> That there is considerable interaction of carbon black with polymer is recognized from the well-known phenomenon of bound rubber.

The amount of work or torque required to maintain constant shear rate while completely dispersing carbon black into polymer is influenced by structure of the black and black-polymer interaction, therefore, this torque is a measure of the reinforcement of polymer providing no polymer breakdown occurs during mixing. The Brabender Plasticorder<sup>14</sup> was utilized to obtain our measurements. This is a small internal mixer equipped with a torque-measuring device with temperature and shear rate controls and gives a direct measure of the amount of torque needed to maintain constant shear rate in the chamber containing the polymer and black.

## EXPERIMENTAL

### A. Mixing and Torque Measurement

A Model PL-V31 Brabender Plasticorder was used in much of the mixing work. This model is equipped with temperature and shear rate controls. The torque measuring head, cam-style, was charged with 42.5 g. of polymer or 33.8 g. of polymer plus 16.9 g. of carbon black. Whenever necessary, preliminary runs were made to determine the temperature designed to give the actual desired batch temperature. Measurement of torque began as

soon as the black was visually incorporated or, if a charging chute was used, when the chute closed tightly. Torque was measured directly on a continuous chart.

### B. Bound Rubber

A sample weighing approximately 0.2 g. was weighed on an analytical balance, cut into several small pieces, and placed into a preweighed, covered wire cage fabricated of 320-mesh stainless steel wire cloth. The cage containing the sample was placed into a 4-oz. stoppered bottle containing 100 ml. of solvent. The sample was stored at room temperature ( $22 \pm 2^\circ\text{C}$ .) for the required period of time (3 days for BR and SBR). The cage containing the bound rubber gel was then removed from the solvent, vacuum-dried at  $50^\circ\text{C}$ . to a constant weight, and then reweighed. Per cent bound rubber was calculated as percentage of rubber bound of the total amount of rubber available:

$$\text{Bound rubber, \%} = [(W_d - F)/R] \times 100$$

$W_d$  = weight of dried gel,  $F$  = weight of filler in gel (same as weight of filler in original sample), and  $R$  = weight of polymer in original sample.

## RESULTS

### A. Polymer Evaluation

The manner or means by which carbon black reinforces polymers is similar, regardless of the polymer, but the measure of this reinforcement as it is determined by interaction and carbon black structure is obscured by changes, caused by high shear stresses, in the polymer itself. Generally, when reinforcing furnace blacks are added to a polymer during the mixing process, the increased viscosity resulting from addition of the black produces higher shear stresses which cause more rapid and greater degrees of polymer breakdown. While this viscosity increase is a measure of reinforcement, the true degree to which the black is effective is masked by changes in the viscosity of the polymer. Therefore, a major prerequisite to measuring reinforcement by carbon blacks is a polymer that does not change in viscosity during the mixing process. The behavior of three polymers during mixing at constant shear rate and at four different temperatures is shown in Figure 1. The reaction of the butadiene rubber (BR) to shear and temperature is seen to be unique. With natural rubber (NR), SBR, and butyl rubber, viscosity of the polymer decreases with mixing, and this change in viscosity is constantly changing with time. Increasing the temperature at which mastication takes place also produces a lower initial viscosity, shown by the intercept on the torque axis at zero time, and leads to changes in the rate at which viscosity decreases. The BR however, is unaffected by mastication or temperature up to a critical level above which polymer breakdown occurs. This breakdown is then in linear relationship with mastication time. With increasing

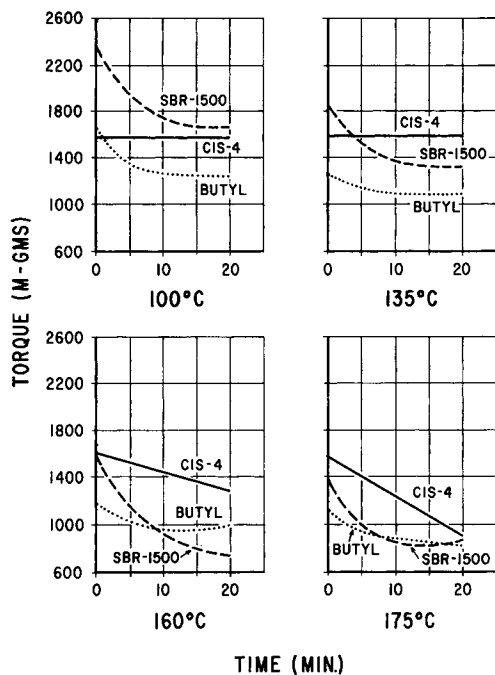


Fig. 1. Effect of temperature and shear on polymer breakdown: (—) *cis*-4; (---) SBR-1500; (...) butyl.

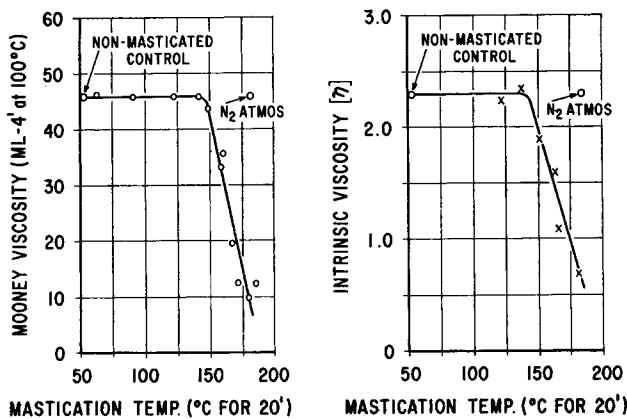


Fig. 2. Mooney viscosity and intrinsic viscosity of masticated butadiene rubber.

temperature the rate of breakdown increases but still appears to be linear with time.

Also to be noted is that, at the temperatures investigated, torque at zero time remains unchanged. The influence of mixing temperature on the Mooney and intrinsic viscosities of BR is shown in Figure 2. These

data are in complete accord with the torque measurements and underline two factors of importance: (1) no change occurs with this polymer as a result of mixing at temperatures less than 148°C. while above this temperature molecular weight of the polymer decreases linearly with temperature; (2) when mastication is conducted in the absence of air, the mixing process no longer produces molecular weight degradation, even if the temperature surpasses the critical level of 148°C.

To complete the picture of the behavior of this polymer, an inert filler was incorporated into BR at 20, 30, 40, and 50 phr loadings. Glass beads (Minnesota Mining and Manufacturing Code 380, 25  $\mu$  diameter) were used. Intrinsic viscosity of the recovered polymer after mixing 20 min. at 110°C. was about 2.8, compared with the control having  $[\eta] = 2.6$ –2.8.

### B. Carbon Black-Polymer Interaction

**Influence of Polymer.** Since the contrasting behavior of raw polymers during mastication at various temperatures has been shown in Figure 1, it is informative to compare the effect of reinforcing furnace carbon black upon the torque requirements for mastication for BR and SBR (Fig. 3).

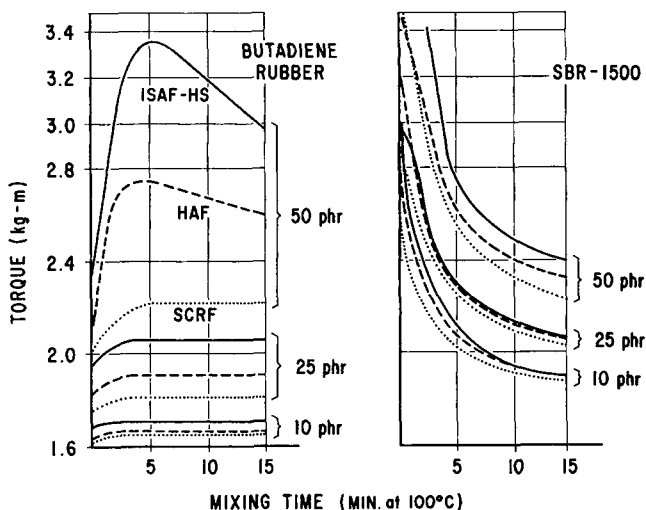


Fig. 3. Effect of black and black loading on mixing in two polymers: (—) ISAF-HS; (---) HAF; (...) SCRF.

The difference in the type of curve obtained with the two polymers is striking. When the polymer matrix decreases in molecular weight with mastication, as in SBR-1500, torque required for mixing the black-polymer mix decreases with time. The torque curves do reflect the difference in level of black, but, except at the highest level (50 phr), do not reflect the vast differences in structure of the three blacks. Considerably greater

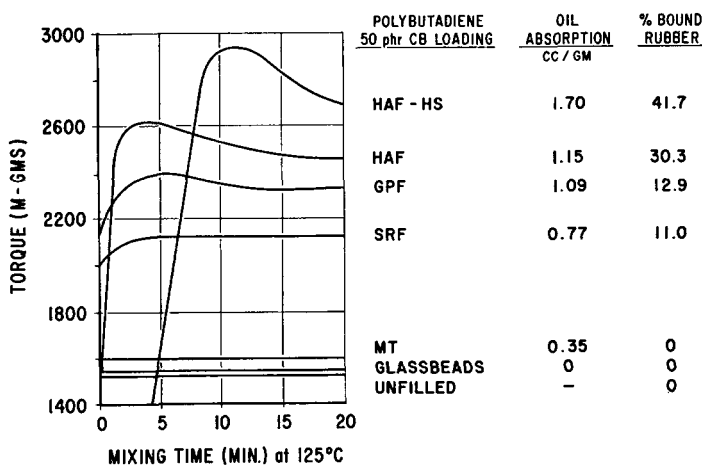


Fig. 4. Reinforcement by carbon blacks as reflected in torque-mixing time curves.

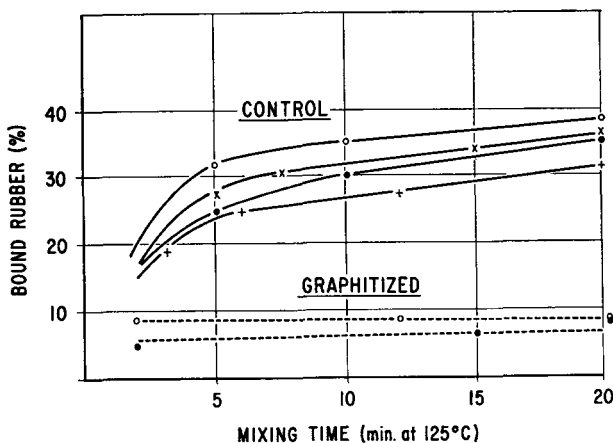


Fig. 5. Bound rubber formation during mixing: (O) ISAF-HS; (●) ISAF; (X) HAF-HS; (+) HAF.

distinction between black type and level is apparent with the use of butadiene rubber. The torque is shown to increase with mixing time rather than decrease, the influence of black level is much more apparent, and, even at the lower black levels, the distinction between different types of black is more obvious. In addition, at the highest black level (50 phr), the influence of carbon black is even further accentuated by the formation of a peak in the torque curve, and the height of this peak seems to reflect the reinforcement qualities of the carbon black. This is more fully shown in Figure 4. Increasing reinforcement potential of the carbon blacks, based upon oil absorption or influence upon Mooney, modulus, or abrasion resistance, is indicated by higher torque level, and, with the blacks of high

reinforcement potential, a peak is obtained in the torque curve. This peak torque is higher and appears later in the torque-time curve with blacks of increasing reinforcement potential.

In spite of the differences in torque curves of the various carbon blacks in the two polymers, it must be that the processes of black incorporation and dispersion are at least similar. However, with SBR-1500, the influence of the carbon black upon mixing torque is obscured by the decreased viscosity of the polymer matrix during mixing. Avoiding this deterioration in molecular weight allows the measurement of the stiffening effect of the carbon black. One means of comparing the similarity of

TABLE II  
Carbon Black-Polymer Interaction and Mooney Viscosity (50 phr Black)

Black	Treatment	Bound rubber, %		MS-4 Mooney viscosity	
		BR	SBR-1500	BR	SBR-1500
ISAF-HS <sup>a</sup>	None	35.5	34.3	80	70
	1200°C.	19.7	20.3	70	69
	Graphitized	7.2	5.6	59	83
ISAF <sup>a</sup>	None	29.1	30.6	61	57
	1200°C.	15.9	18.3	56	58
	Graphitized	5.3	5.8	52	67
ISF-LS <sup>b</sup>	None	13.7	16.8	47	54
	Graphitized	5.1	6.4	48	56
SCRFB <sup>b</sup>	None	27.8	28.1	57	55
	Graphitized	4.3	7.5	49	59
Thermal <sup>b</sup>	None	0	0	33	37
	Graphitized	0	0	28	31
HAF-HS <sup>b</sup>	None	35.9	32.0	60	55
	Graphitized	7.1	7.3	55	62
ISAF <sup>b</sup>	None	38.7	33.3	57	50
	Graphitized	6.6	7.8	51	59

<sup>a</sup> Mixing time, 15 min.

<sup>b</sup> Mixing time, 20 min.

interaction during the mixing processes in BR and SBR is to measure the bound rubber formed during mixing of the carbon black. The bound rubber found with various carbon blacks in SBR and BR is shown in Table II. It is evident that differences in interaction of polymers with these carbon blacks are minor. The development of bound rubber during mixing with CIS-4 polybutadiene\* is shown in Figure 5.

This interaction between carbon black and polymers has been found to increase slightly with increased mixing temperature. It has also been found that this increased interaction is reflected in increased torque level during mixing in polybutadiene where the polymer does not undergo serious molecular weight degradation during the process (Fig. 6). The

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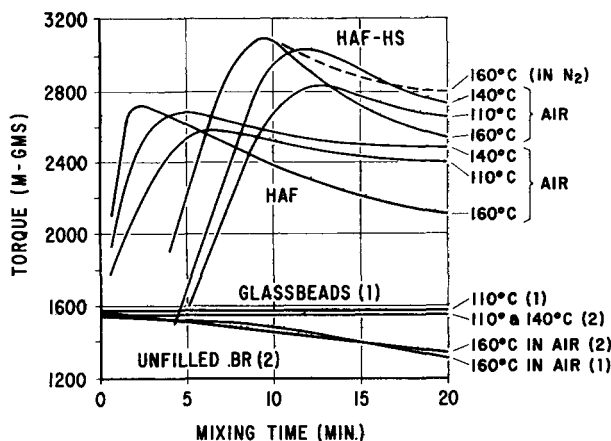


Fig. 6. Carbon black-polymer interaction at three temperatures as shown by mixing torque requirements.

higher structure black shows higher peak torque compared with the normal structure carbon black, and with increasing mastication temperature this peak torque increases and is achieved earlier in the mixing cycle. It is interesting to observe that the whole curve for 140°C. is above that for 110°C., whereas normally viscosity decreases as the temperature is raised. This is due to the increased interaction at the higher temperature. Increasing the temperature above the critical level (148°C.) does not change the influence of increased interaction upon peak torque but it is instead reflected in the more rapid decrease in torque level in the later stages of mixing after peak torque has been passed.

**Effect of Black Treatment.** The formation of bound rubber by interaction between carbon blacks and polymers is the result of specific surface activity of the carbon black particle. Thus, it may be produced by either physical-type or chemical-type bonding, or both. Different bonding may depend upon type of carbon black, and treatment of black-polymer during the mixing step. Independent of its mechanism of formation, it has a physical effect upon the composition of the mixture—a portion of the rubber has been effectively removed as part of the matrix and added to increase the filled volume portion.

As the specific surface activity is reduced by heat treatment,<sup>15</sup> a drastic reduction in bound rubber formation is noted (Table II and Fig. 5), while surface area and oil absorption show only slight changes. During the process of mixing carbon black in polymers, bound rubber increases rapidly during the early stages, then tends to level off and increase slowly in a relationship more linear to time. The more reinforcing carbon blacks form higher amounts of bound rubber, and the linear portion of the curve is seen to occur later in the mixing cycle. The graphitized blacks all form very early approximately the same level of bound rubber that re-

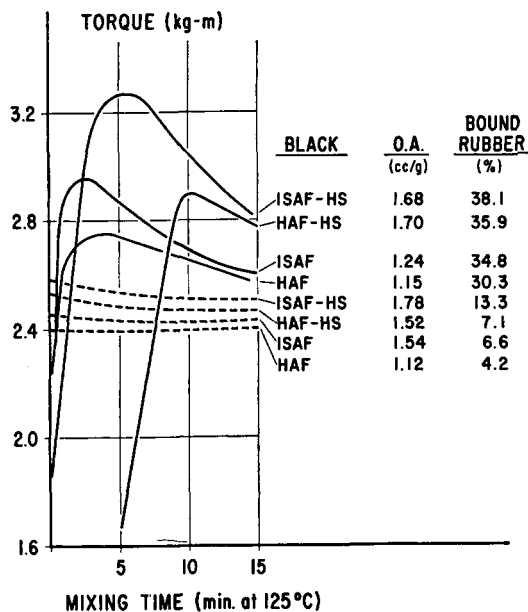


Fig. 7. Effect of graphitization on interaction and torque in polybutadiene rubber: (—) control blacks; (---) graphitized blacks.

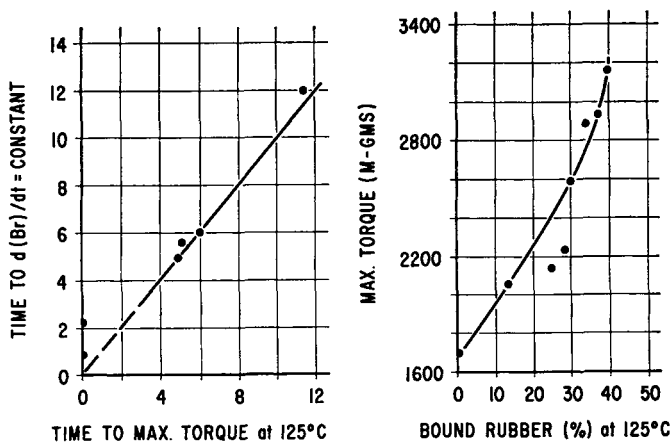


Fig. 8. Interrelation of torque and bound rubber.

mains essentially constant during subsequent mixing. This interaction of carbon black with polymer is measured by the work necessary for mixing, represented by torque level and the presence of a peak in the torque curve, as shown in Figure 7. Only the torque-time curves for the reinforcing furnace carbon blacks show a distinct peak torque. The peak is highest for the blacks with the higher bound rubber and occurs later in the mixing cycle. Graphitized carbon blacks have such low specific surface activity

and so decrease bound rubber formation that no peak in the torque curve occurs and actually the torque required for mixing is considerably lower than that of the original blacks.

A direct correlation can be shown between rate of bound rubber formation and the presence of a peak in the torque required for mixing by comparing the time at which peak torque occurs with the time at which rate of bound rubber formation becomes linear (Fig. 8a). Further, the amount of bound rubber formed has an influence upon the torque requirements of mixing and shows a correlation with the height of the torque maximum (Fig. 8b).

The shape of the torque versus mixing time curves of Figure 6 and 7 has been adequately explained up to the maximum. The occurrence of the maximum and the subsequent downward trend of the curve must be attributed to another factor opposed to the stiffening effect of the bound rubber formation.

For this decrease there may be two reasons: (1) notwithstanding all the evidence that the polybutadiene as such does not break down under shear, it may still degrade to some extent in the presence of carbon black; (2) the structure of the black itself which still has some influence on the compound viscosity may break down during mixing. There is direct evidence that the latter is the case with high-structure blacks. The carbon black was recovered from the mixture by pyrolyzing the rubber and oil absorption, as a measure of structure, determined for the recovered black. Results are given in Table III. With the lower structure blacks this effect is less pronounced and may not be measurable. It is significant that the slope of the curve after the maximum in the torque-time curve is most pronounced with the high-structure blacks, due to this breakdown in black structure.

TABLE III  
High Structure ISAF in SBR-1500

Mixing time, min.	Oil absorption, cc./g.
0	1.7
3	1.5
6	1.4
12	1.34
20	1.3

### C. Effect of Black Surface Activity on Rubber Properties

The extent to which this potential enhancement of mechanical properties of a rubber compound is maintained throughout the necessary processing steps so that full advantage of the reinforcing potential of the carbon black is attained is of primary importance in the achievement of improved physical properties. Some insight into the reasons why the expected reinforcement is not always achieved may be gained by following

the influence of carbon black-polymer interaction upon some selected physical properties.

**Viscosity Effects.** An indication of the significance of the bound rubber is obtained through the application of the Guth-Gold equation to carbon black-filled polybutadiene

$$M = M_0 (1 + 2.5C + 14.1C^2)$$

By defining the parameter  $C$  for volume fraction of filler not as carbon black alone but as carbon black plus bound rubber, we are able to calculate a Mooney viscosity from carbon black loadings and the measured corresponding bound rubber content (Table IV).

Agreement between measured and calculated Mooney is good with the graphitized carbon black except at the highest loadings. With the non-graphitized control, agreement is less satisfactory (Table IV). The measured values are lower than those calculated since measurements were made after 20 min. of mixing when the torque had decreased considerably from its maximum value. Mooney viscosity measured at the peak of the torque-time curve would give better agreement with the calculated curves. With the graphitized blacks, no peaks occur in the torque curves and in these cases the agreement between calculated and measured viscosities is satisfactory.

TABLE IV  
Mooney Viscosity of Carbon Black-Butadiene Rubber Compounds  
(Mixed at 130°C. for 20 min.)

Black	Black level		Bound rubber, %	Filled volume fraction, %	MS-4		
	phr	vol.			Measured	Calc. for total filled volume (black + bound rubber)*	Calc. for black volume only*
ISAF-HS	2	1.08	0	1.01	32	28	28
	10	5.38	0	4.82	37	31	31
	30	16.1	27.2	37.4	57	100	42
	40	21.6	34.2	43.2	90	120	48
	50	26.7	35.9	49.0	102	150	52
	60	32.3	46.0	59.0	170+	200	63
HAF- Graphi- tized	10	5.38	0	4.82	33	31	31
	20	10.8	0	9.2	40	36	—
	30	16.1	4.5	19.1	46	48	42
	40	21.6	6.1	23.0	55	60	48
	50	26.7	8.0	26.5	65	68	52
	60	32.3	7.5	28.8	77	74	63
	70	37.6	4.9	29.7	94	76	—
	80	43.0	7.2	34.0	113	90	76

\* MS =  $MS_0 (1 + 2.5C + 14.1C^2)$ ;  $MS_0 = 26$ .

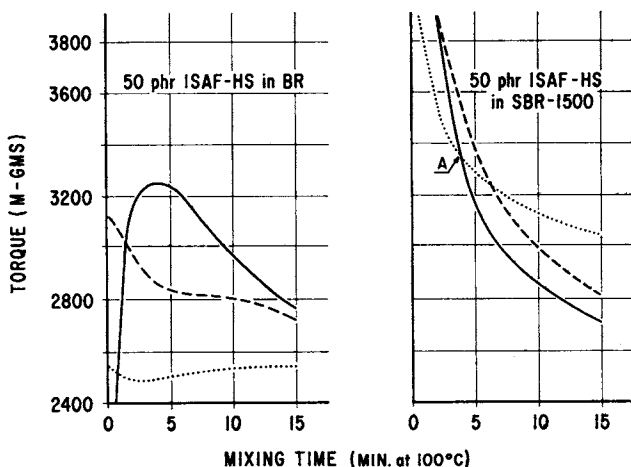


Fig. 9. Effect of carbon black-polymer interaction upon polymer breakdown during mixing: (—) control black; (---) heat treated at 1000°C.; (···) graphitized.

The values in Table IV calculated from the volume fraction of black alone (without the bound rubber) deviate considerably from the measured values for both types of black. From another perspective, the agreement between measured and calculated Mooney with the graphitized black is added indication that the polymer does not break down in molecular weight during mixing at this temperature (130°C.).

Additional insight of the influence of bound rubber was obtained by comparison of the Mooney viscosities of carbon black reinforced BR and SBR-1500 for compounds with several different carbon blacks (Table II). As shown previously, the extent of interaction of each black with both polymers is in every case equivalent; however, with any carbon black the Mooney viscosities of the BR compounds increase with bound rubber, while in contrast Mooney viscosities of SBR-1500 compounds decrease as also illustrated by the torque curves of Figure 3. The incorporation of highly reinforcing furnace black and the subsequent high level of interaction produces initially a very viscous compound (Fig. 9). A higher torque is required to mix a more viscous compound at a constant rate of shear; this higher torque results in a greater amount of work being applied to the polymer and, thus, with SBR-1500 a greater amount of polymer breakdown. A low degree of interaction, shown by heat-treated blacks, leads to less viscous stock initially, and the lower torque requirement for mixing produces less polymer degradation. When polymer degradation is avoided, Mooney viscosity increases with increased interaction.

At a point A where the torque values of the compounds of regular and graphitized black in SBR-1500 are equal (Fig. 9), there must be another reason for the faster breakdown of the control compound. This control contains a larger proportion of bound rubber which may not be subject

to an equivalent degree of breakdown, but acts as part of the filler so that practically all the shear is exerted on a smaller amount of matrix than in the case of the graphitized black. It is also possible that the control black enhances the polymer breakdown catalytically.

At the crossover point we apply the Einstein-Guth and Gold equation for both the regular and the graphitized black compound, although this is not strictly correct in view of the rather high rate of shear employed here. Then indexing the graphitized compound with 1 and the regular compound with 2 one obtains for viscosity  $V$ :

$$V = V_{01} (1 + 2.5C_1 + 14.1C_1^2) = V_{02} (1 + 2.5C_2 + 14.1C_2^2)$$

or

$$V_{01}/V_{02} = (1 + 2.5C_2 + 14.1C_2^2)/(1 + 2.5C_1 + 14.1C_1^2)$$

The per cent bound rubber for regular black is 25% and for graphitized black is 9.0% for a 50 black phr compound. Therefore, the volume fraction of filler plus bound rubber,  $C$ , are found to be

$$C_1 = 0.27$$

$$C_2 = 0.40$$

and

$$V_{01}/V_{02} = 4.25/2.75 = 1.55$$

Assuming that this represents the ratio of viscosities of the nonbound polymer in the two compounds, this is related to its weight-average molecular weight by the equation:<sup>19</sup>

$$M_1/M_2 = (V_{01}/V_{02})^{.3} = (1.55)^{.3} = 1.14$$

The intrinsic viscosities of the extract resulting from the bound rubber determination were then measured (in benzene at 25°C.). These represent the molecular weights of the polymer not bound to black. The values obtained were:

$$I_1/I_2 = 2.03/0.66 = 3.1$$

Since<sup>20</sup>  $I_1/I_2^{1.5} = M_1/M_2$ , one obtains  $M_1/M_2 = (3.1)^{1.5} = 5.5$ , so, obviously, there is no satisfactory agreement with  $M_1/M_2$  calculated from the Einstein-Guth and Gold equation using the volume of bound rubber as an added part of the filler volume.

Therefore, with SBR-1500 one must conclude that other unknown factors play the important part in determining the mixing torque at this high rate of shear.

**Modulus Effects.** Because it has many times been found to reflect the abrasion-resistant qualities of a black, a widely accepted criterion of reinforcement is modulus. Compounds were prepared for vulcanization with SBR and BR polymer by mixing for different periods of time to attain

different levels of black-polymer interaction (Table V). Cure times were selected to reach equivalent crosslink density, measured by swelling in *n*-heptane. When polymer degradation does not occur during the mixing process, modulus and tensile increase with mixing time or extent of interaction; when polymer degradation does occur, modulus decreases at the lower elongation.

TABLE V  
Carbon Black-Polymer Interaction and Modulus (50 phr HAF)<sup>a</sup>

Polymer	Mixing time, min.	Bound rubber, %	Modulus, psi			Tensile strength, psi	Elongation, %
			100%	200%	300%		
SBR-1500	1	12.1	717	1636	2623	2743	300
	2	15.0	605	1537	2627	3125	340
	3	16.9	580	1574	2643	3805	400
	5	19.3	524	1431	2492	3692	410
	10	22.5	518	1509	2663	4049	420
	15	24.4	542	1518	2684	4011	410
BR	1	12.7	433	957	1668	1900	310
	2	15.0	438	969	1739	2153	340
	3	15.1	421	957	1718	2148	330
	5	17.1	455	1012	1827	2096	330
	10	19.7	450	1053	1891	2462	330
	15	21.5	447	1046	1896	2703	390

<sup>a</sup> Compounding recipe: polymer 100 parts, black 50 phr, ZnO 3.0 phr, stearic acid 1.5 phr, softener 8.0 phr, sulfur 1.75 phr, Santocure 1.25 phr, antioxidant 1.0 phr.

**Effect on Cure Level.** A more fundamental influence of carbon black-polymer interaction is noted in cure level. It has long been known that reinforcing furnace carbon blacks lead to so-called excess crosslinks.<sup>16</sup> This is the crosslink density, measured by swelling, of the matrix of a vulcanizate containing highly reinforcing carbon black compared with the crosslink density of an identically cured gum vulcanizate or one containing nonreinforcing carbon black or filler. It is possible to show that the bound rubber as a result of interaction is a factor in the presence of this excess crosslink density as it has been shown to be a factor in Mooney viscosity. Identically cured vulcanizates were prepared containing 50 phr HAF high structure, HAF, and SCF blacks. In addition to the controls, the blacks were heat-treated at 500, 1000, 1500°C., and graphitization temperature to change the extent of interaction with polymers. The swelling of the cured gum,  $V_{r0}$ , is compared with the swelling of an identically cured carbon black-reinforced polymer,  $V_r$ , as a ratio,  $V_{r0}/V_r$ . The influence of carbon black activity and bound rubber is depicted by using as the filled volume the volume fraction carbon black plus volume fraction bound rubber ( $\phi$ ). The data (Fig. 10) show that at constant loading increasing interaction produces an increasing proportion of excess crosslinks. The changes are similar to those shown by Kraus<sup>17</sup> in his development of a

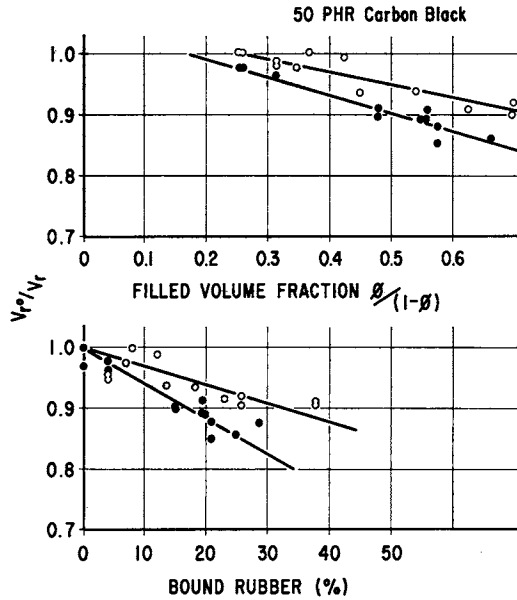


Fig. 10. Correlation of excess crosslinks with bound rubber: (●) SBR; (○) BR.

relationship covering effect of volume fractions of carbon black upon excess crosslinks.

#### D. Reinforcement in Blends

Of considerable interest at the present time is the use of blends of BR and SBR-type polymers to utilize the superior wearing qualities of the

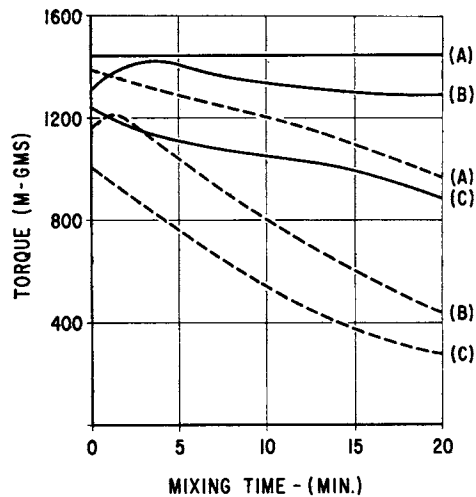


Fig. 11. Influence of mixing time and temperature on polymer and polymer blends: (A) butadiene rubber; (B) SBR-1710; (C) blend; at (—) 115°C. mixing; (---) 160°C.



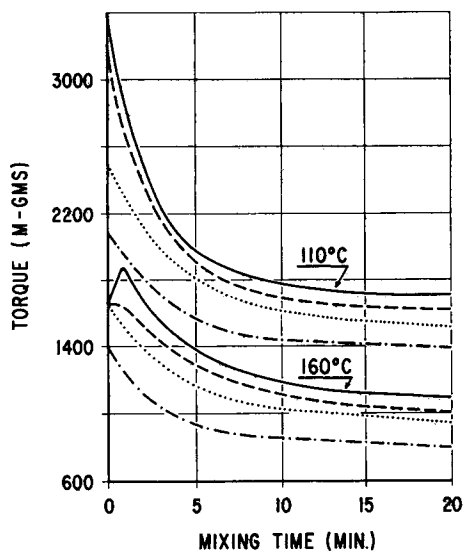


Fig. 12. Effect of carbon black and temperature on polymer breakdown during mixing of OEP-BR blends: (—) ISAF-HS; (---) HAF-HS; (...) HAF; (-·-) SCRF.

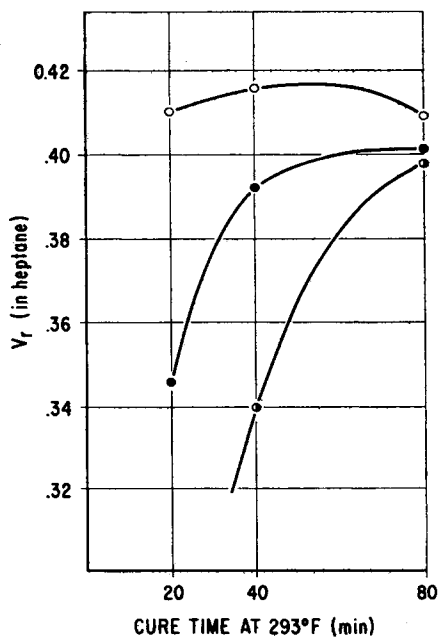


Fig. 13. Cure rate of polymer and polymer blends containing 50 phr ISAF carbon black: (○) BR; (●) Blend 50/50; (●) SBR-1500.

stereoregular polymer while still maintaining acceptable processing and mixing characteristics. It has often been found that the full advantages of the wearing qualities of the stereoregular polymer have not been gained. The information gathered about reinforcement by carbon black has been applied to the problems of polymer blends.

The curves of torque versus time for the individual polymers and the blend (Fig. 11) and for the blend with four different blacks (Fig. 12) show that the behavior of the SBR polymer during mixing is the major influence upon the shape of the torque curve and indicates a marked decrease in the molecular weight of the SBR polymer. This decrease in molecular weight will change with different carbon blacks, being greater for the more reinforcing blacks and the extent, of course, depending upon time of mixing. It is obvious, therefore, that, in attempting to compare the wearing qualities of blends reinforced with different carbon blacks and mixed for equal lengths of time in factory equipment, the comparisons are generally invalidated since the vulcanizates are not based upon equivalent rubber compounds. If blending is not complete, we may have separate SBR and polybutadiene phases on a small scale. As the bound rubber builds up the polybutadiene becomes more stiff, whereas the SBR phase will break down, widening the gap in viscosity between these two phases. This may result in poor properties and lack of reproducibility of test results. These differences and changes during mixing and processing are further emphasized when cure rate and level of the individual polymers are considered (Fig. 13). The BR cures rapidly and completely in a low sulfur recipe,<sup>18</sup> and, when vulcanized in the same recipe as normally used with SBR-1500, the polymers in the blend must be at much different states and level of cure. Consideration of the  $V_r$  data of the blend suggests that the BR will be in a state of overcure while the SBR probably never reaches optimum cure.

## CONCLUSIONS

Using as the rubber matrix a polymer that does not break down in molecular weight or Mooney viscosity during the mixing process, the force required to disperse a carbon black into a polymer is an indication of the reinforcing potential of the carbon black. The interaction between carbon black and polymer is represented by other amount of bound rubber produced during the mixing process, and the amount of bound rubber can be correlated with the torque requirements for this mixing process. This interaction is also shown to influence Mooney viscosity, modulus, and cure level. If a polymer matrix such as SBR is used, which does degrade during mixing with shear stresses or temperature, the influence of interaction between carbon black and polymer upon rheological and physical properties is obscured to a considerable degree.

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## Résumé

L'interaction du noir de carbone avec les hauts polymères pendant le processus de mélange a été étudiée en employant des charges ayant un large domaine de caractéristiques de surface. Des perles de verre, du graphon, du carbone hautement structuré, du carbone traité par la chaleur ont été mélangés avec des élastomères dans un Brabender Plasticorder. En employant comme matrice de caoutchouc un haut polymère qui ne change pas matériellement de poids moléculaire ou de viscosité pendant le mélange, une excellente corrélation a été trouvée entre le couple de torsion final, requis pour mélanger, et la structure du carbone, et d'autre part entre le couple maximum et le caoutchouc environnant. Un accroissement de l'interaction allait de pair avec un accroissement du couple au moment du mélange, un accroissement de la viscosité selon Mooney, un accroissement du module, et un état de vulcanisation plus élevée, mesurée, par gonflement. Quand la matrice de haut polymère casse au cours du mélange, ces influences d'interaction sont généralement obscurcies par une diminution de poids moléculaire.

## Zusammenfassung

Die Wechselwirkung von Russ mit Hochpolymeren während des Mischungsvorganges wurde unter Verwendung von Füllstoffen mit einem weiten Bereich an Oberflächencharakteristika untersucht. Glaskugeln, Graphon, Hochstrukturusse und hitzebehandelte Russe wurden in einem Brabender Plasticorder mit Elastomeren gemischt. Bei Verwendung eines Hochpolymeren, das während des Mischungsvorganges weder Molekularge-

wicht noch Viskosität beträchtlich ändert, als Kautschukmatrix wurde zwischen dem Enddrehmoment für die Mischung und der Russstruktur einerseits und zwischen Maximaldrehmoment und gebundenem Kautschuk andererseits eine ausgezeichnete Korrelation gefunden. Es zeigt sich, dass eine Zunahme der Wechselwirkung zu einer Zunahme des Mischdrehmoments, der Mooney-Viskosität, des Moduls und zu einem höheren, durch Quellung gemessenen, Vulkanisationsgrad führt. Wenn die Hochpolymermatrix während des Mischungsprozesses zerstört wird, so sind diese Wechselwirkungseinflüsse meist durch Abnahme des Molekulargewichts verdeckt.

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